Calorimetric observations of amorphous and crystalline Ni-Zr alloy formation by solid-state reaction

E. J. Cotts,* G. C. Wong,† and W. L. Johnson
Keck Laboratory, California Institute of Technology, Pasadena, California 91125
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Differential scanning calorimetry and x-ray diffraction are utilized in a study of solid-state vitrification of multilayered composites of Ni and Zr. In order to understand better and optimize the amorphizing reaction, we have examined the kinetics of competing reactions: the formation and growth of crystalline intermetallic compounds. The value of the activation energy, E_c, of the initial crystallization of the growing amorphous phase is determined to be $E_c = 2.0 \pm 0.1$ eV, establishing an upper limit on the thermal stability of the amorphous-diffusion couple.

Numerous layered composities of polycrystalline elements will intermix and form new phases when heated above room temperature. For Ni/Zr composites at low temperatures ($T \leq 600$ K) and short diffusion distances ($x \leq 1000$ Å), an amorphizing reaction[1,2] controls the kinetics and final product of the mixing of the layers.[3–7] This amorphizing reaction must be faster than alternative reactions which lead to equilibrium compounds. The reaction to the metastable amorphous phase has been shown to be driven by a large negative free energy of mixing which substantially reduces the driving force for the formation of stable phases.[6,7] At relatively short diffusion distances the growth of the amorphous phase is diffusion limited, and thus the rate of growth continually slows.[6,7] Eventually a stable crystalline phase becomes kinetically favored and begins to grow. In order to understand better and optimize the amorphizing reaction, we have examined the kinetics of the competing reactions: the formation and growth of crystalline intermetallic compounds. These solid-state reactions are directly monitored by differential scanning calorimetry.[6,7]

Elemental foils of Zr and Ni (99.9% purity, 26 μm thick) were consolidated by means of cold rolling in stainless-steel sheaths.[8] A constant rolling direction (within 5°) was maintained during repeated passes through a rolling mill. The degree of deformation of the composite is characterized by the reduction ratio (RR), where RR is equal to $(i/f)2^n$, with i the initial composite thickness, f the final composite thickness, and n the number of times the composite is doubled over on itself between passes through a rolling mill. For ideal deformation, the thickness of an individual layer in the multilayered composite is its initial thickness divided by the RR. In practice, a distribution of layer thicknesses exists and the RR is simply a qualitative indication of the degree of reduction of individual layer thicknesses.[8] A sample of given RR was removed from the stainless-steel sheath, characterized by means of x-ray diffraction, and then cut into a number of similar, smaller samples to facilitate analysis by differential scanning calorimetry (DSC). All samples for DSC scans were hermetically sealed in aluminum pans by cold welding in an inert atmosphere. Each DSC scan was followed immediately by a second scan (identical thermal conditions) of the same sample; the data from the second scan were subtracted from the data from the first scan. A Perkin-Elmer DSC-4 interfaced to an Apple IIE computer was utilized for DSC measurements. A Norelco x-ray diffractometer with Ni filtered, Cu $K\alpha$ radiation was used for obtaining x-ray diffraction (XRD) profiles of the materials.

The effect of an increasing degree of deformation of the composites upon the course of a subsequent solid-state reaction is illustrated in Fig. 1. A series of DSC scans at

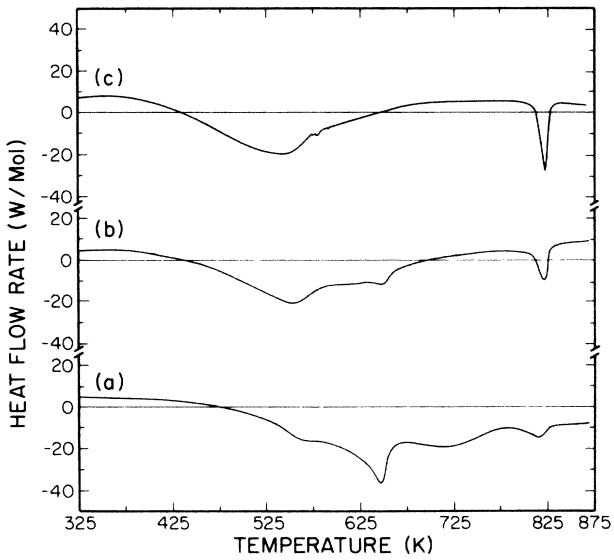

FIG. 1. The heat-flow rate as a function of temperature for a constant scan rate of 10 K/min, measured by means of differential scanning calorimetry. The samples were multilayered composites of Ni and Zr of average stoichiometry $Ni_{66}Zr_{34}$, produced by co-deformation of the two metals. The data are for samples of increasing degree of deformation. (a) The least deformed sample of reduction ratio RR of 10^2. (b) Sample with a RR of 10^3. (c) The most deformed sample with a RR of 10^4.

constant heating rate (10 K/min) are displayed for composites (average stoichiometry $Ni_{66}Zr_{34}$) of increasing RR. The DSC scan for the least deformed sample [Fig. 1(a)] reveals a broad exothermic signal at temperatures below 625 K that we associate with the intermixing of the Ni and Zr layers to form amorphous material. An XRD profile of a similar sample which was heated in the differential scanning calorimeter to 600 K and quenched to room temperature reveals a broad band of x-ray intensity centered at $2\theta \cong 40°$ [Fig. 2(b)] which is not observed in XRD scans of similar samples in the as-rolled condition [Fig. 2(a)]. The broad band in Fig. 2(b) is similar to those observed in XRD profiles of liquid-quenched metallic glasses of approximate composition $Ni_{60}Zr_{40}$, which supports the contention that the heat release observed below approximately 600 K in these DSC scans corresponds to the formation of amorphous phases.[5–7,9]

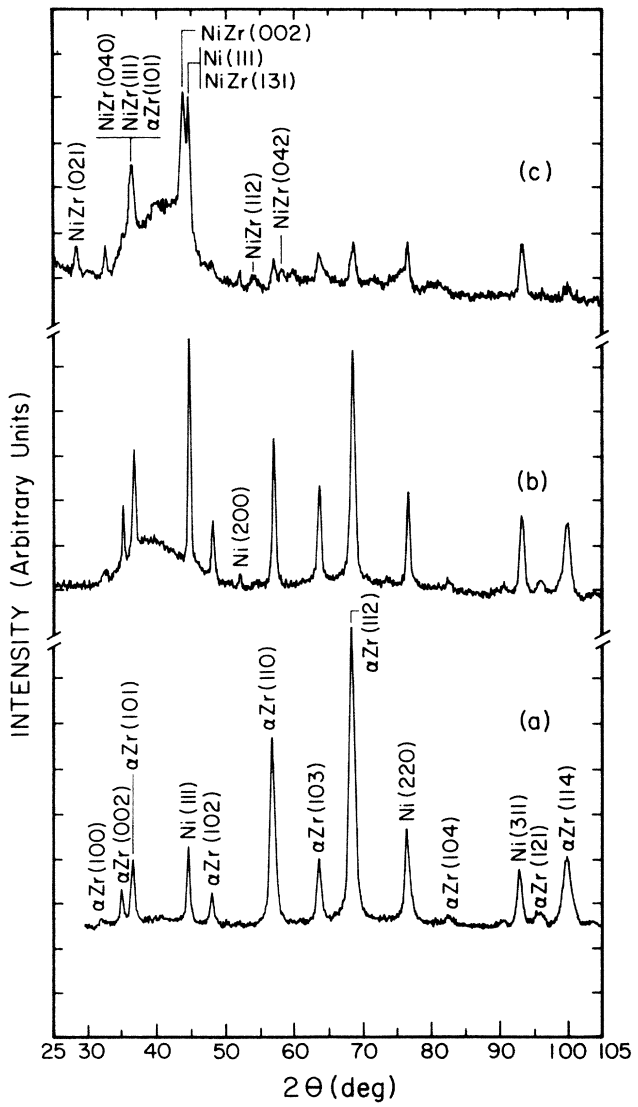

FIG. 2. X-ray diffraction profiles (Cu $K\alpha$ radiation) for the bulk sample of Fig. 1(a), a multilayered composite of Ni and Zr of average stoichiometry $Ni_{66}Zr_{34}$. (a) The as–co-deformed sample. (b) The sample after being heated at 10 K/min to a temperature of 600 K and quenched to room temperature in the differential scanning calorimeter. (c) The sample after being heated at 10 K/min to a temperature of 675 K and quenched to room temperature in the differential scanning calorimeter.

Upon examining Ni/Zr composites of various compositions and RR's, we observe a correlation between an exothermic peak at 650 K in DSC scans (10 K/min) and the appearance in XRD scans of Bragg peaks which can be indexed with an orthorhombic NiZr phase of approximate composition $Ni_{50}Zr_{50}$.[10] For instance, an XRD profile [Fig. 2(c)] of a sample with a RR of 10^2 heated in the differential scanning calorimeter at 10 K/min to 675 K [cf. Fig. 1(a)] and quenched to room temperature reveals, in addition to a broad band at $2\theta \cong 40°$ associated with amorphous material, the presence of new Bragg peaks associated with orthorhombic Ni-Zr.

Previous studies[10,11] have shown that amorphous material is formed in these amorphizing reactions with a linear composition gradient between endpoint compositions of $Ni_{68}Zr_{32}$ and $Ni_{47}Zr_{53}$. Furthermore, the crystallization temperatures of liquid-quenched Ni/Zr metallic glasses in this composition range have been reported to decrease essentially monotonically with decreasing Ni content.[12,13] The most Zr-rich material (approximate composition $Ni_{47}Zr_{53}$) in the amorphous diffusion couple is found at the Zr interface, where nucleation sites for crystallization are provided, and would be expected to crystallize at a lower temperature than the rest of the diffusion couple.[10,11] The growth of orthorhombic Ni-Zr at the Zr interface in these diffusion couples has in fact been previously observed by means of transmission electron microscopy after annealing at 573 K for between 5 and 12 h.[14,15] The crystalline Ni-Zr was observed to have grown forward into the Zr, with a small amount of the amorphous material consumed. Thus, we associate the sharp exothermic peak observed at 650 K in DSC scans (10 K/min) of these Ni/Zr composites with the formation and growth of the intermetallic compound Ni-Zr at the interface between the crystalline Zr and the amorphous material.[16] In general, such an exothermic peak in a DSC scan of Ni/Zr multilayers signals the end of the solid-state amorphization reaction. Subsequent annealing results only in the production of crystalline material.

The production of composites suitable for obtaining complete solid-state amorphizing reactions can be optimized through characterization of composites by means of DSC. In Fig. 1 it is observed that upon increasing the RR (decreasing layer thickness) the broad exothermic peak observed in DSC scans, which is associated with the growth of the amorphous phase, increases in magnitude. Furthermore, at an RR of 10^4 [Fig. 1(c)], no crystallization peak is observed at 650 K. A XRD profile [Fig. 3(b)] of a sample with a RR of 10^4 heated at 10 K/min to 675 K and quenched to room temperature reveals a broad XRD peak centered at $2\theta \cong 41°$ and weak Bragg peaks corresponding to elemental Ni, with no Bragg peaks corresponding to any intermetallic compounds or elemental Zr. Such an observation is consistent with the previous observation[14,15] that crystalline Ni-Zr nucleates and grows at the Zr-rich, amorphous-alloy/crystalline-Zr interface. Thinner individual layers in composites of in-

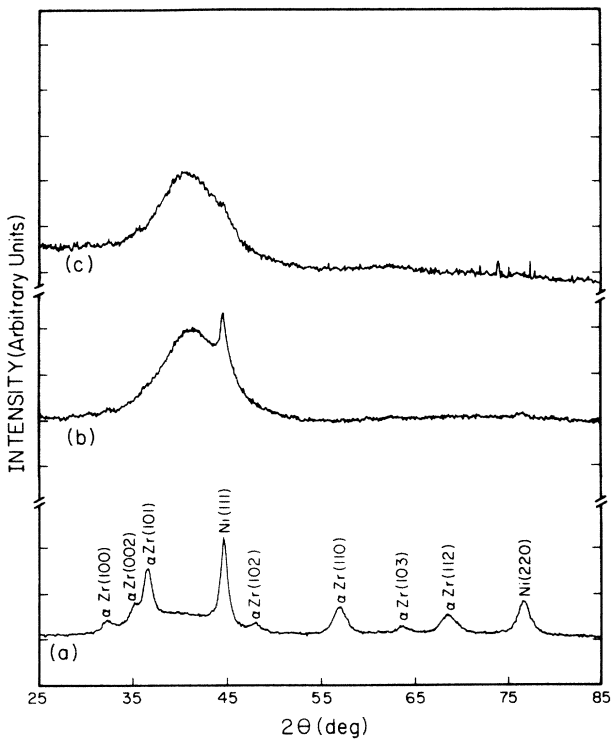

FIG. 3. X-ray diffraction profiles (Cu $K\alpha$ radiation) for the bulk sample of Fig. 1(c), a multilayered composite of Ni and Zr of average stoichiometry $Ni_{66}Zr_{34}$. (a) The as–co-deformed sample. (b) The sample after being heated at 10 K/min to a temperature of 675 K and quenched to room temperature in the differential scanning calorimeter. (c) The sample after being annealed at a temperature of 600 K for 4 h and quenched to room temperature.

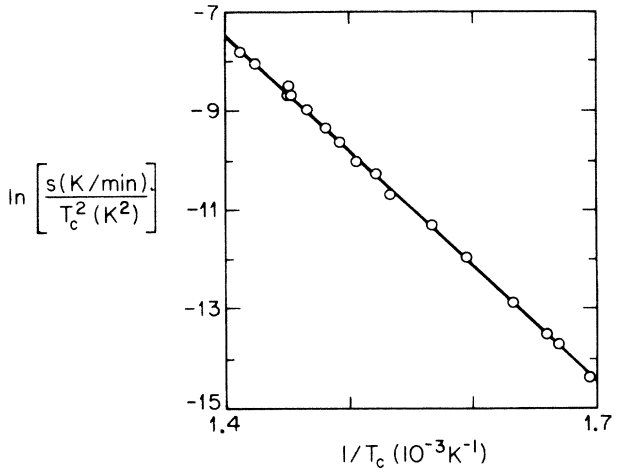

FIG. 4. The natural logarithm of the heating rate, s, divided by the square of the crystallization temperature, T_c, vs the inverse crystallization temperature. The solid line is a least-squares fit to the data points.

creasing RR accommodate the consumption of Zr at lower temperatures (i.e., temperatures below ≈ 625 K) such that the nucleation and growth of orthorhombic Ni-Zr is by-passed. Similar samples with a RR of 10^4 annealed at 600 K for extended times (4 h) can be essentially completely amorphized, as evidenced by XRD profiles [Fig. 3(c)].

The kinetics of the initial crystallization process was studied by monitoring the temperature of the formation of orthorhombic Ni-Zr, T_c. The values of T_c were determined from the maximum of exothermic peaks, which had been correlated with the formation of crystalline Ni-Zr by means of XRD and (based on the results of a different study[15]) transmission electron microscopy, for a series of DSC scans of various heating rates (0.2–200 K/min). Kissinger's method[17] (Fig. 4) was utilized to determine the activation energy, E_c, for the initial formation and growth of orthorhombic Ni-Zr to be $E_c = 2.0 \pm 0.1$ eV. The observed value of E_c is significantly higher than the activation energy, E_a, for interdiffusion in the early or middle stages of the growing amorphous phase[7,11,18] ($E_a = 1.1$ eV). The observed value of E_c is less than the reported activation energies of crystallization of liquid-quenched metallic glass of compositions close to $Ni_{47}Zr_{53}$ (3.5 eV for $Ni_{45}Zr_{55}$, 2.4 eV for $Ni_{50}Zr_{50}$, and 2.9 eV for $Ni_{52}Zr_{48}$).[12,13] The initial crystallization of the growing amorphous phase occurs at a temperature approximately 50° below the crystallization temperature of liquid-quenched metallic glass of composition near $Ni_{47}Zr_{53}$.[12,13] The data obtained for the slowest DSC scan rates (e.g., 0.2–2.5 K/min) overlap the time and temperature regime of previous isothermal annealing experiments involving transmission electron microscopy,[15] where orthorhombic Ni-Zr was observed to have grown forward into the crystalline Zr without significant growth back into the amorphous phase. These observations are consistent with nucleation and growth of crystalline Ni-Zr at the Zr interface of the diffusion couple.

The disparity between the values of E_c and E_a implies that amorphous growth should be favored at lower temperatures, as is observed. The observation that at a temperature of 593 K the amorphous interlayer can be grown to a maximum thickness of 950 Å would imply that amorphous layers of thickness on the order of 10^4 Å could be grown at still lower temperatures, but only a very weak temperature dependence of the maximum amorphous layer thickness has been observed.[15] The implication is that for long times and/or large thicknesses, the average interdiffusion coefficient D in the growing amorphous phase decreases. A smaller value of D would limit the growth of the amorphous interlayer in the time before the nucleation and growth of crystalline Ni-Zr occurs. In fact, previous observation has revealed evidence that D decreases at long times and large thicknesses of the growth of amorphous material.[19–21]

The thermal stability of the amorphous phase at the Zr interface determines an upper limit for the stability of the amorphous Ni/Zr diffusion couple. The observed values

of T_c and E_c are consistent with the contention that heterogeneous nucleation of crystallites in the growing amorphous phase occurs at the Zr interface. Based on these results, the production of metallic glasses by means of solid-state reaction can be better understood and optimized by examining existing thermal stability data gathered for liquid-quenched metallic glasses and by characterization of diffusion couples by means of DSC.

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*Permanent address: Physics Department, University Center at Binghamton, State University of New York, Binghamton, NY 13901.

†Permanent address: Physics Department, University of California at Berkeley, Berkeley, CA 94720.

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